

THE CHEMISTRY OF TELLURIC ACID

by

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B. A., Adams State College, 1953

A THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1955



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INTRODUCTION

Telluric acid, although not a new compound, has not been extensively studied. Several preparations for the compound have been investigated which are based on the oxidation of either the free element, or one of the compounds of a lower oxidation state. The methods for a quantitative analysis are not comprehensive and are usually rather long and tedious.

Probably the most widely accepted preparation is that of Mathers and co-workers, which is based on the action of potassium permanganate in an acid medium, on tellurium dioxide (10). This method gives a very good yield of the crude product, but some of the impurities which are inherent in the preparation must be eliminated by further chemical action on the product. The method of Meyer and Franke (11) of oxidizing the free element with chloric acid, has given yields of ninety to ninety-five percent. However, the number of reaction products formed leads to a large number of impurities which must be eliminated. There are also a number of variations of these procedures, although basically they all consist of the action of a strong oxidizing substance on metallic tellurium or tellurium dioxide (1, 5, 7, 12).

Gutbier and Wegenknecht (5), in 1904, described a preparation of the acid in which they oxidized tellurium dioxide in a strongly basic medium with 15 percent hydrogen peroxide. To a hot (70° C) mixture of tellurium dioxide and 30 percent potassium hydroxide, a 15 percent

solution of hydrogen peroxide was added and the mixture boiled. During the boiling, more peroxide was added and a vigorous evolution of gas took place. The tellurium dioxide all went into solution and was oxidized to telluric acid. This solution was filtered, acidified with nitric acid, and cooled. Upon cooling, large crystals of the acid were obtained. These were filtered, washed in a nitric acid solution and dried with a water bath. After recrystallizing this product three times, the purity was about 99.9 percent as shown by results obtained on reduction of the acid with hydrazine hydrochloride.

The preceding method was to be used in the preparation of the telluric acid for this investigation. The results that were obtained in this laboratory did not agree with those described by Gutbier. The procedure was then investigated further and a modification of this process was obtained. The major change made in the procedure was to change the concentration of the sodium hydroxide and the hydrogen peroxide. Results were then obtained which gave a product favorable to use in further studies.

Quantitative analysis of telluric acid has been investigated by several different methods, although most of these methods are rather bulky and hard to handle. The most widely accepted method at present is that of Gooch and Howland (4). This method consists of the reduction of the telluric acid to tellurous acid by potassium bromide in a strongly acid medium. A sample of the acid is placed in a round-bottom flask along with sulfuric acid and an excess of potassium bromide. The volume

is then adjusted to approximately 250 ml. and the reaction vessel and condenser are swept free of air by carbon dioxide, which is continually bubbled through the solution during the reaction. As the mixture is heated, the reaction takes place liberating free bromine which is distilled into a beaker containing a solution of potassium iodide. The adapter on the condenser is kept below the surface of the potassium iodide solution thereby eliminating loss of bromine. The iodine which is liberated by the bromine is then titrated by a standard solution of sodium thiosulfate using starch solution as the indicator. This method gave very good results and was used to check the purity of the acid which was prepared by the procedure investigated in this laboratory. Lingane and Niedrach (9) used a procedure which involved the potentiometric titration of the +6 tellurium with chromous ion. This method did not work very well, as the temperature was a deciding factor. The reaction mixture had to be kept at an elevated temperature during the entire titration. Rosenheim and Weinheber (14) used glycerol to complex the acid. This effectively caused the acid to behave as a monobasic acid and it could then be titrated by ordinary means using phenolphthalein as the indicator. This method gave results ranging from 96.87 percent to 103 percent for a single sample. Another method was devised by Lenher and Homberger (8) which involved the reduction of the acid by hydrazine salts. This method, however, did not give good results as the reaction is not completely quantitative.

Since the ultraviolet absorption spectrum for the tellurate ion is different from that of telluric acid (Stuber, et al. 16), Scott and Leo-

nard (15) developed a spectrophotometric method for the microdetermination of telluric acid. This method involved the determination of a plot of absorbance versus concentration of a series of standard solutions of telluric acid. The concentration of an unknown solution was then determined by comparison of its absorbance with the standardization curve. In order to extend the useful concentration range, the possibility of a spectrophotometric titration was investigated. A solution of telluric acid was titrated using sodium hydroxide, and the reaction followed spectrophotometrically. Investigation of this procedure showed that due to the strong absorption of carbonate and silicate ions, this type of titration was not feasible. Carbonate free sodium hydroxide was tried also, but the results were erratic and non-reproducible. Ammonium hydroxide was then tried and proved to work out very successfully. Although the volatility of ammonium hydroxide makes it a rather poor standard, it was carefully stoppered and checked frequently. There seemed to be no noticeable change in concentration over a months time. The results obtained were precise and reproducible. The method is fast and the presence of strong acids did not interfere with the determination. The plot of the ml. of base added versus the absorbance gave very sharp breaks and extrapolation of the curves for the endpoint was easily accomplished.

EXPERIMENTAL

Apparatus

A Beckman Model DU spectrophotometer with a flame attachment was used for the analysis of sodium as an impurity in the crude telluric acid. The same spectrophotometer equipped with an ultraviolet light source and quartz cells was used for the analytical determination of the acid.

Chemicals

Reagent grade chemicals were used without further purification except for the tellurium dioxide and the telluric acid which was prepared by the procedure described in this thesis.

Since the tellurium dioxide contained such impurities as manganese, iron, and other metallic elements, it was purified in the following manner. Four hundred grams of tellurium dioxide and 217.6 grams of sodium hydroxide pellets were mixed together in a three-liter beaker. Then 750 ml. of distilled water was added in 250 ml. portions, waiting each time until the reaction subsided. The mixture was stirred well and heated for one hour before filtering. The resulting mixture was filtered once through E & D 612 filter paper and twice through Whatman #42 filter paper. The solution was then diluted to 1600 ml. and nitric

acid (1:1) was added with stirring, until there was about 50 ml. in excess. This took approximately 650 ml. of the acid. The precipitate was allowed to stand for one hour and decanted. The residue was washed with water by decantation until the solution no longer tested acid. It was filtered through E & D 612 and dried in an air oven at 100 degrees centigrade. The yield was about 95 percent.

Preparation of Telluric Acid

Five hundred ml. of a solution of hydrogen peroxide and sodium hydroxide, made by adding equal volumes of 30-percent hydrogen peroxide and 10-percent sodium hydroxide, was blended at a rate which maintained a vigorous reaction with the tellurium dioxide in a three liter beaker. The beaker was kept over a low flame during the blending to insure that the reaction went to completion. After the reaction had subsided, 50 ml. of concentrated nitric acid was added and the solution was allowed to stand overnight. The crystals were filtered and air dried for one hour at room temperature. The yield of the acid was around 95 percent of the theoretical yield.

Purification of the crude acid was carried out by successive crystallizations. The first crystallization was carried out from a dilute solution of nitric acid, while the second and third crystallizations were carried out in a water solution. The yield of pure acid will vary according to the number of recrystallizations and the method used, since

approximately nine grams of telluric acid will dissolve in 100 ml. of water at zero degrees centigrade and 230 grams will go into solution at 100 degrees centigrade. For every one hundred grams of crude acid to be purified, approximately 70 ml. of hot water was used to put all of the acid into solution. The resulting solution was then evaporated until the first crystals of acid began to appear. The solution was then cooled. After the solution had cooled to room temperature, the crystals were filtered and air dried at room temperature for one hour. After the third recrystallization of the acid, the yield was about 80 percent of the starting material.

Quantitative Analysis of Telluric Acid

A ten-milliliter sample of the telluric acid stock solution was placed in a 250-ml. erlenmeyer flask and 40 ml. of water added. An eyedropper was then used to transfer this solution to a one-centimeter quartz cell. With water as a blank, the absorbance was read and recorded. The sample of the acid was then returned to the titrating flask by the same method of transfer. A small amount of standardized ammonium hydroxide was then added to the flask, the contents stirred thoroughly, and a sample transferred to the quartz cell. After each addition of base, some of the solution was used to rinse the cell, and then a sample was transferred to the cell and the absorbance determined. This process was continued for the entire titration. During

the titration, the flask was placed in a water bath maintained at 20 degrees centigrade. The cell compartment of the spectrophotometer was equipped with a set of thermospacers and the temperature of the compartment was maintained at 20 degrees. The absorbance was plotted versus the ml. of base added. This type of titration gave a very smooth curve which was easily extrapolated to give the stoichiometric point of the reaction. Klingman, et al. (6) have shown in a recent article a modification of the cell compartment of a Beckman Model DU spectrophotometer which would speed up the titration as used in this investigation.

RESULTS AND DISCUSSION

Although the method as described by Gutbier and Wegenknecht (6) used a 30-percent solution of either sodium or potassium hydroxide, the results obtained in this laboratory by this procedure gave unsatisfactory results. The data indicated that the ratio of the concentration of base to the concentration of hydrogen peroxide was the determining factor in the oxidation. When the reaction was carried out in an extremely basic solution, such as that used by Gutbier and Wegenknecht, all that was obtained was an extremely gummy substance that was insoluble in acids, bases and 30-percent hydrogen peroxide. If a very low concentration of base was used, then the tellurium dioxide failed to go into solution and the reaction was not carried to completion.

When the concentration of the final solution was adjusted to be 5-percent sodium hydroxide and 15-percent hydrogen peroxide, the reaction went to completion. The yield of telluric acid was from 1.3 to 1.4 grams of telluric acid per gram of tellurium dioxide oxidized. This was very near the theoretical yield.

The impurities in the acid prepared by this method should largely be sodium nitrate and nitric acid. These impurities were easily removed by recrystallization from water, due to their extreme solubility. A study of the removal of sodium ion was carried out using the Beckman Model DU Flame Photometer. Sodium chloride was used to prepare a series of standards which were used to make a standardization curve. The samples of telluric acid were made in the following manner. A sample of the supernatant liquid and some of the precipitate were taken from the original precipitation. The acid was then recrystallized from a dilute nitric acid solution and another sample taken of the supernatant liquid and the precipitate. This method of sampling was carried out for a total of five crystallizations. The supernatant liquid was used directly while one gram of the wet acid was dissolved in 25 ml. of distilled water. Table 1 shows the results of the removal of sodium ion from these solutions.

Table 1. Concentration of sodium ion in the supernatant liquid and the precipitate after each recrystallization.

| Sample | Concentration of Na ⁺ in ppm. | | | | |
|--------------------|--|------|-----|-----|-----|
| | Original | 1st | 2nd | 3rd | 4th |
| Supernatant liquid | >1000 | 400 | 25 | 20 | 12 |
| Precipitate | 21.2 | 11.5 | 3.5 | <1 | <1 |

The results from this study show that the ease and completeness of removal of sodium ion is accomplished by three recrystallizations.

Several methods were tried for the analysis of telluric acid. The first method was that of titrating the acid with a standard base and following the reaction with a pH meter. As shown by Fig. 1, the break in the curve corresponding to the titration of the first hydrogen is not steep enough to give a satisfactory endpoint either with the pH meter technique or with an internal indicator. Also, the break occurs a little above the theoretical point for the first hydrogen, possibly indicating partial titration of a second replaceable proton. The next method investigated, was a conductimetric titration of the telluric acid with a standard sodium hydroxide solution (Fig. 2). A precipitation of barium tellurate involving the use of a standard barium chloride solution was followed conductimetrically without usable results. Also, the possibility of precipitating cupric tellurate from an ammoniacal copper solution was studied. The cupric ammonia complex was found to be stable enough to prevent precipitation of the tellurate.

The shift of the telluric acid ultraviolet absorption spectrum upon the addition of a base was studied. A standard solution of sodium hydroxide was prepared carbonate free and a sample of the telluric acid was titrated with the base and followed spectrophotometrically. Although this investigation indicated that spectrophotometric methods might be used, the results obtained using sodium hydroxide were erratic and non-reproducible. Carbonate-free sodium hydroxide as well as a

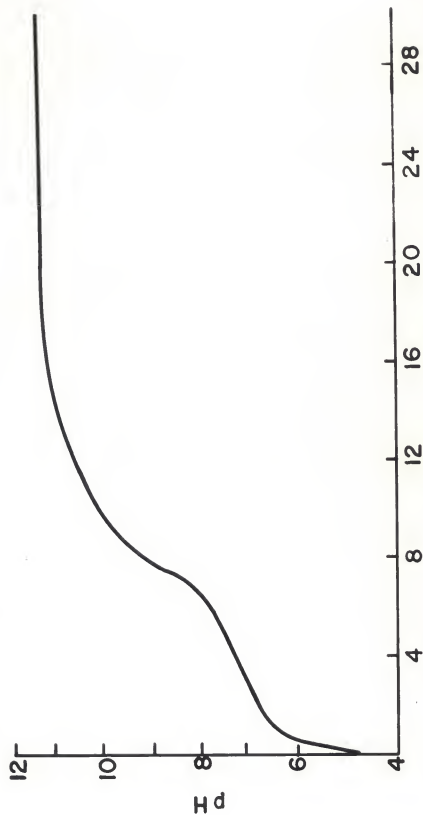


Fig. 1. Titration of ,1008 M H_6TeO_6 vs. ,1332 M NaOH.

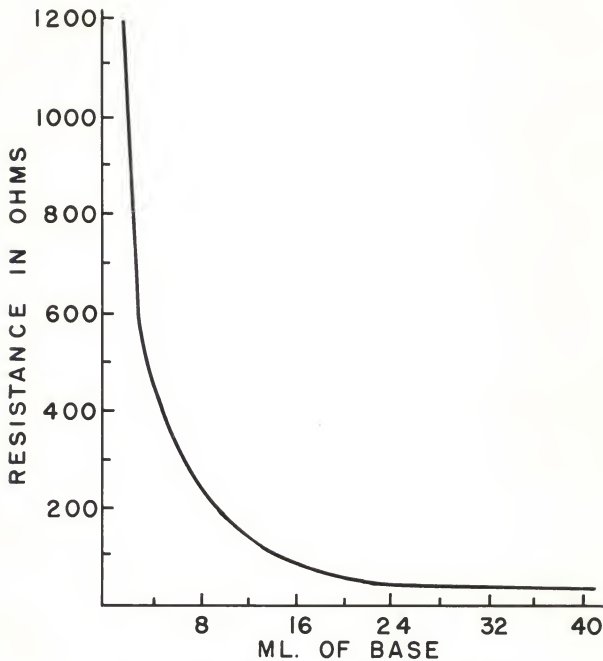


Fig. 2. Conductimetric titration of telluric acid.
10 ml. of .1008 M H_6TeO_6 vs. .1687 M NaOH.

solution of sodium hydroxide which contained carbonate were tried. As shown by Table 2, the results from either solution were extremely poor.

Table 2. Results obtained using sodium hydroxide as the standard base.

| Number | Milligrams of acid added | Milligrams of acid found | Error |
|--------|-----------------------------|-----------------------------|---------|
| 1* | 445.5 | 584.0 | + 138.5 |
| 2* | 107.9 | 234.3 | + 126.4 |
| 3* | 3.79 | 4.47 | + 0.68 |
| 4** | 107.9 | 115.9 | + 8.00 |
| 5** | 107.9 | 92.30 | - 15.60 |
| 6** | 107.9 | 102.9 | - 5.00 |

* Carbonate free

** Contain carbonate

The carbonate-free sodium hydroxide seemed to give the poorest results, while the solution containing carbonate ion did not seem to follow a given pattern of error. Results from the latter solution gave both high and low results, although they were closer to the true value than those obtained with the carbonate-free base.

The titration of telluric acid with ammonium hydroxide was studied. The volatility of ammonium hydroxide did not interfere with its use as a standard solution. During the investigation, the strength of the base

was constantly checked and it was found that there was no apparent change in the standardization of the solution. Since the ammonium hydroxide titration with telluric acid gave reproducible results and sharp, distinct breaks even in the most dilute concentration range of telluric acid, ammonium hydroxide was the base which was finally used for the entire analysis.

The change in absorbance during the titration was observed at various wavelengths as shown in Fig. 3. The complete study showed that for the concentrations of the acid used in this investigation 270 millimicrons gave the best results. The lower limit for this concentration was 260 millimicrons, while the upper limit appeared at 300 millimicrons. Beyond these limits no curves were obtained which gave breaks that could easily be extrapolated to indicate the endpoint.

A study of the effect of concentration (Table 3) revealed that by changing the wavelength the titration was useful for a concentration range between 445.5 milligrams and 11.25 milligrams. From the results obtained for this concentration range, the best wavelength would be close to 270 millimicrons for the 445.5 mgm. samples and as the concentration of the acid decreased, lower wavelengths were necessary to assure adequate adsorption. The concentration of base with respect to the concentration of the acid should be in the range of three to one. Keuffel and Esser 10 x 10 to the half-inch graph paper was used to plot the results. The plotting of these curves was one of the factors which had a great influence on the amount of error. Use of this paper allowed plotting to the limit of the accuracy of the buret which was used.

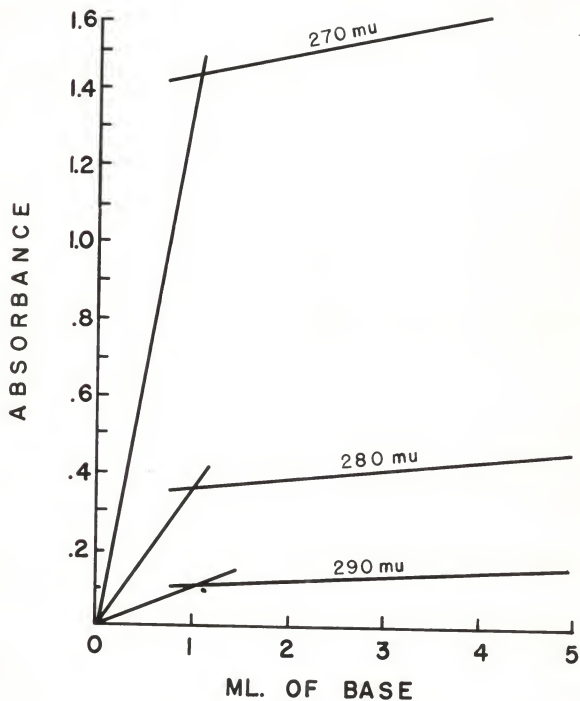


Fig. 3. Effect of wavelength. 10 ml. of .2 M H_6TeO_6 vs. 1.937 M NH_4OH .

Table 3. Concentration effects on the determination of telluric acid.

| Wavelength in millimicrons | : Milligrams of acid added | : Milligrams of acid found | : Error in milligrams |
|-------------------------------|-------------------------------|-------------------------------|--------------------------|
| 300 | 445.5 | 442.6 | + 2.9 |
| 290 | 445.5 | 447.1 | + 1.6 |
| 280 | 445.5 | 445.5 | 0.00 |
| 270 | 445.5 | 447.1 | + 1.6 |
| 270 | 222.5 | 223.5 | + 1.0 |
| 270 | 222.5 | 223.8 | + 1.3 |
| 270 | 112.5 | 114.8 | + 2.3 |
| 270 | 112.5 | 112.3 | - 0.2 |
| 270 | 56.12 | 54.90 | - 1.24 |
| 260 | 31.23 | 31.12 | - 0.11 |
| 250 | 11.25 | 11.25 | 0.00 |

The buret was graduated in hundredths of a milliliter and could be estimated to the thousandth of a milliliter. As is shown by the curves, there is very little change in absorbance until all of the other acids have been titrated.

Interference studies on the titration of telluric acid in the presence of other strong or weak acids was carried out at a wavelength of 270 millimicrons. Figures 4 and 5 show the general type of curve obtained when telluric acid is titrated in the presence of other acids. Only those acids which possibly would be expected to be present in tellurium samples, or those acids which were introduced in various phases

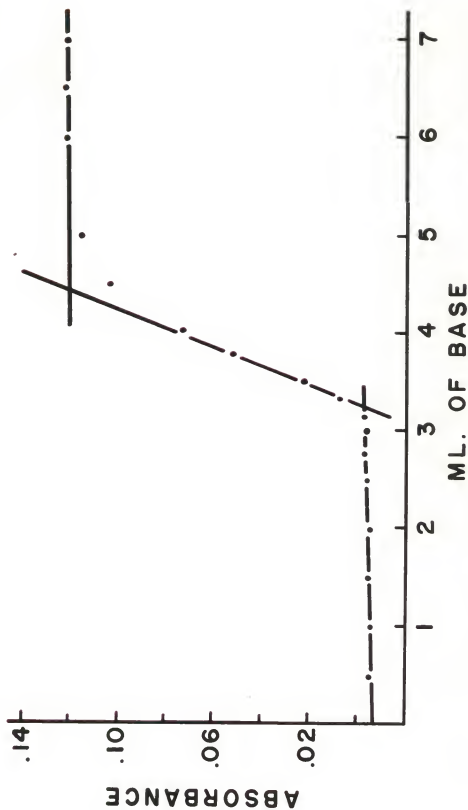


Fig. 4. Ten ml. of .05 M $\text{H}_2\text{C}_2\text{O}_4$ vs. .470 M NH_4OH in the presence of H_2SO_4 .

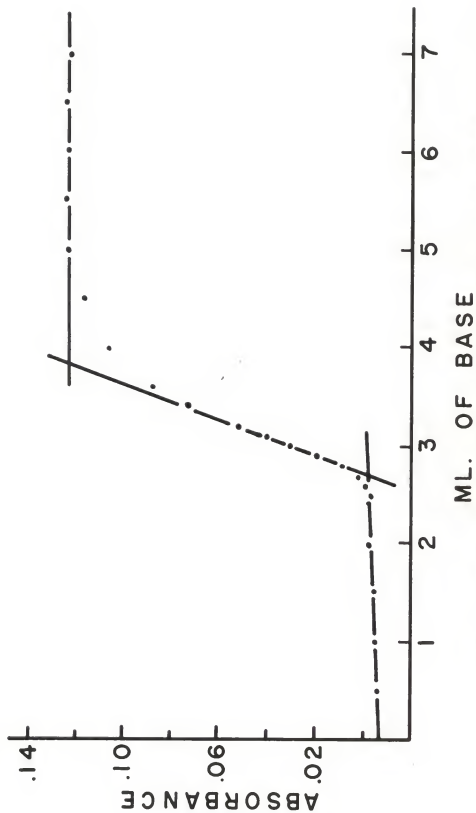


Fig. 5. Ten ml. of .05 M H_6TeO_6 vs. .470 M NH_4OH in the presence of $\text{HC}_2\text{H}_3\text{O}_2$.



of the preparation were used in the interference study. Table 4 shows the results obtained in the determination of telluric acid in the presence of various other acids. The dilution factor $\frac{V + N}{V}$ (2) proposed by Goddu and Hume was applied to all of the titrations involved in the interference study. Acetic acid was used to show the effects of a weak acid. Of the five acids used in the interference study, only nitric acid, which absorbs in this region of the spectrum, was found to interfere. With the exception of the nitric acid in this study, the mean deviation was 0.35 mgm.

Table 4. Interference study in the analysis of telluric acid.

| Interference | : Milligrams of : acid added | : Milligrams of : acid found | : Error in : mgm. |
|---|---------------------------------|---------------------------------|----------------------|
| HCl | 107.9 | 107.7 | - 0.2 |
| HNO ₃ | 107.9 | 105.1 | - 2.8 |
| H ₂ SeO ₄ | 107.9 | 107.9 | 0.0 |
| H ₂ SO ₄ | 107.9 | 108.6 | + 0.7 |
| HC ₂ H ₃ O ₂ | 107.9 | 108.5 | + 0.6 |

CONCLUSION

Telluric acid may easily be prepared in good yield and purity by the method described in this paper. The use of hydrogen peroxide in a

weakly alkaline medium greatly reduces the number of impurities in the preparation, and the impurities that are present are easily and effectively removed by recrystallization of the acid from water.

Spectrophotometric analysis of telluric acid may be accomplished by titration of the acid with a solution of ammonium hydroxide. A plot of absorbance versus ml. of base added is easily extrapolated to determine the endpoint of the reaction. The method is fast, accurate, and precise.

ACKNOWLEDGMENT

The author wishes to express his thanks to Dr. G. W. Leonard for his help in making this work possible.

BIBLIOGRAPHY

1. Gilbertson, L. I.
A method of preparation of telluric acid. J. Am. Chem. Soc. 55:1460-1461. 1933.
2. Goddu, R. F., and D. N. Hume.
Photometric titrations of weak acids. Anal. Chem. 26:1679-1684. 1954.
3. Goddu, R. F., and D. N. Hume.
Photometric titrations. Anal. Chem. 26:1740-1745. 1954.
4. Gooch, F. A., and J. Howland.
An iodometric method for the estimation of telluric acid. Am. J. Sci. (3) 48:375-378. 1894.
5. Gutbier, A., and W. Wegenknecht.
On the influence of hydrogen peroxide on tellurium dioxide: A new method of preparation of telluric acid. Z. Anorg. allgem. Chem. 40:260-263. 1904.
6. Klingman, D. W., D. T. Hooker, and C. V. Banks.
Photometric titration assembly for Beckman Model DU spectrophotometer. Anal. Chem. 27:572. 1955.
7. Krepelka, J. H., and L. Kubik.
The preparation and determination of pure orthotelluric acid from metallic tellurium. Chem. Listy. 42:28-30. 1948.
8. Lenher, V., and A. W. Homberger.
The gravimetric determination of tellurium. J. Am. Chem. Soc. 30:387-391. 1908.
9. Lingane, J. J., and L. Niedrach.
Potentiometric titration of +4 and +6 selenium and tellurium with chromous ion. J. Am. Chem. Soc. 70:1997-2000. 1948.
10. Mathers, F. C., C. M. Rice, H. Broderick, and R. Forney.
Inorganic Syntheses. Vol. III. First Edition. New York: McGraw Hill Book Co., Pages 145-147. 1946.
11. Meyer, J., and W. Franke.
Preparation of telluric acid. Z. Anorg. allgem. Chem. 193: 191-192. 1930.

12. Meyer, J., and H. Moldenhauer.
Preparation of telluric acid. A. Anorg. allgem. Chem. 119:
132-134. 1921.
13. Pascal, P., and M. Patry.
Telluric acids. Compt. Rend. 200:708-711. 1935.
14. Rosenheim, A., and M. Weinheber.
Gravimetric determination of tellurium and the alkalimetric de-
termination of telluric acid. Z. Anorg. allgem. Chem. 69:
266-269. 1910.
15. Scott, L. W., and G. W. Leonard.
A spectrophotometric determination of telluric acid. Anal.
Chem. 26:445-446. 1954.
16. Stuber, C., A. Braid, and G. Jander.
The color and state of tellurium compounds in solutions of varying
pH. Z. Physik Chem. A171:320-330. 1930.

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AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the
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In order to study a compound, it would be necessary to be able to prepare the compound in a pure state and to analyze the compound quantitatively. With this in mind, a modification of one of the earlier preparations was obtained which gave a product of high yield and purity. A quantitative analysis of the product was then worked out which gave good results as well as being fast and accurate.

The preparation consisted of an oxidation of tellurium dioxide in a weakly alkaline medium by use of hydrogen peroxide. The procedure permitted the preparation of a product in a high yield with the number of impurities cut to a minimum. Sodium ions, the main impurity, was easily eliminated from the compound by recrystallization from water. The yield of the crude product was 95 percent of theoretical yield.

Quantitative determination is accomplished by titrating the acid with a standard solution of ammonium hydroxide. The reaction was followed with a Beckman Model DU Spectrophotometer in the ultraviolet range of light. Quartz cells were used and the temperature maintained at 20 degrees centigrade. A plot of the absorbance versus the ml. of base added was made and extrapolated to the stoichiometric point of the reaction. Since the acid exhibits a wavelength change in the presence of a base, no indicators were needed to determine the endpoint.

The yield of acid in the preparation is 95 percent and after three recrystallizations, the yield of purified product was approximately 80 percent. A study of the sodium impurity showed that after three recrystallizations from water, the sodium was effectively removed. The ini-

tial precipitate of the acid contained more than 20 ppm. of sodium ion and after the third crystallization, the concentration of sodium ion was less than one part per million.

In the analysis of the acid, such things as the wavelength, concentration, and interference were studied. The wavelength must be changed according to the concentration of the acid present. The range of concentrations which may be determined is wide and for the most part, good results were obtained over the entire range. The telluric acid may be quantitatively determined with good results in the presence of other strong or weak acids. The method is fast, accurate, and precise.

